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(54) **NONAQUEOUS SECONDARY BATTERY SEPARATOR AND NONAQUEOUS SECONDARY BATTERY**

(57) An object of the invention is to provide a separator for a nonaqueous secondary battery, which has good adhesion to electrodes and is also capable of ensuring sufficient ion permeability even after attachment to electrodes. The separator for a nonaqueous secondary battery of the invention includes a porous substrate

and an adhesive porous layer that is formed on at least one side of the porous substrate and contains a polyvinylidene-fluoride-based resin. The separator for a nonaqueous secondary battery is characterized in that the adhesive porous layer has a crystal size of 1 to 13 nm.

EP 2 696 392 A1

Description

Technical Field

5 **[0001]** The present invention relates to a separator for a nonaqueous secondary battery and also to a nonaqueous secondary battery.

Background Art

10 **[0002]** Nonaqueous secondary batteries, such as lithium ion secondary batteries, have been widely used as power supplies for portable electronic devices such as laptop computers, mobile phones, digital cameras, and camcorders. Further, these batteries are characterized by having high energy density, and thus the application to automobiles and the like has also been studied in recent years.

15 **[0003]** With the reduction in size and weight of portable electronic devices, the outer casing of a nonaqueous secondary battery has been simplified. At first, a battery can made of stainless steel was used as an outer casing, and then an outer casing made of an aluminum can was developed. Further, a soft pack outer casing made of an aluminum laminate pack has also been developed nowadays. In the case of a soft pack outer casing made of an aluminum laminate, because such an outer casing is soft, a space may be formed between an electrode and a separator during charging and discharging, causing a technical problem in that the cycle life is reduced. In terms of solving this problem, a technique for attaching an electrode and a separator together is important, and a large number of technical proposals have been made.

20 **[0004]** As one of the proposals, a technique of using a separator including a polyolefin microporous membrane, which is a conventional separator, and a porous layer made of a polyvinylidene-fluoride-based resin (hereinafter sometimes referred to as an adhesive porous layer) formed thereon is known (see, e.g., Patent Document 1). When such an adhesive porous layer with an electrolyte contained therein is stacked on an electrode and heat-pressed, the electrode and the separator can be well joined together, allowing the adhesive porous layer to function as an adhesive. As a result, it is possible to improve the cycle life of a soft pack battery.

25 **[0005]** In addition, in the case where a battery is produced using a conventional metal can outer casing, electrodes and a separator are stacked together and wound to produce a battery element, and the element is enclosed in a metal can outer casing together with an electrolyte, thereby producing a battery. Meanwhile, in the case where a soft pack battery is produced using a separator like the separator of Patent Document 1 mentioned above, a battery element is produced in the same manner as for the battery having a metal can outer casing mentioned above, then enclosed in a soft pack outer casing together with an electrolyte, and finally subjected to a heat pressing process, thereby producing a battery. Thus, in the case where a separator including an adhesive porous layer as mentioned above is used, it is possible to produce a battery element in the same manner as in the battery having a metal can outer casing mentioned above. This is advantageous in that there is no need to greatly change the production process for conventional batteries having a metal can outer casing.

35 **[0006]** Against the background mentioned above, various technical proposals have been made in the past for separators made of a polyolefin microporous membrane and an adhesive porous layer stacked thereon. For example, in terms of achieving both the ensuring of sufficient adhesion and ion permeability, Patent Document 1 presents a new technical proposal focusing on the porous structure and thickness of a polyvinylidene-fluoride-based resin layer.

Prior Art Documents

Patent Documents

45 **[0007]** Patent Document 1: Japanese Patent No. 4127989

Summary of the Invention

50 Problems that the Invention is to Solve

[0008] Incidentally, the positive electrode or negative electrode of an ordinary nonaqueous secondary battery includes a current collector and an active material layer that is formed on the current collector and contains an electrode active material and a binder resin. In the case where the adhesive porous layer mentioned above is joined to such an electrode by heat pressing, the layer adheres to the binder resin in the electrode. Therefore, in order to ensure better adhesion, the larger the amount of the binder resin in the electrode, the better.

[0009] However, in order to further increase the energy density of a battery, it is necessary to increase the content of the active material in the electrode, and the lower the binder resin content, the better. Therefore, according to the prior

art, in order to ensure sufficient adhesion, it has been necessary to perform heat pressing under severe conditions, such as higher temperatures and higher pressures. Further, according to the prior art, in the case where heat pressing is performed under such severe conditions, there is a problem in that the porous structure of the adhesive porous layer made of a polyvinylidene-fluoride-based resin is destroyed. This results in insufficient ion permeability after the heat pressing process, and it thus has been difficult to obtain good battery characteristics.

[0010] In addition, although a polyvinylidene-fluoride-based resin has been commonly used as a binder resin for use in an electrode, in recent years, it is also becoming common to use styrene-butadiene rubber. In the case where such styrene-butadiene rubber is used in an electrode, when the separator has a conventional adhesive porous layer, it has been difficult to obtain sufficient battery characteristics achieving both ion permeability and adhesion.

[0011] Against such a background, an object of the invention is to provide a separator for a nonaqueous secondary battery, which has better adhesion to electrodes compared with the prior art and is also capable of ensuring sufficient ion permeability even after attachment to an electrode.

Means for Solving the Problems

[0012] In order to solve the problems mentioned above, the invention is configured as follows.

1. A separator for a nonaqueous secondary battery, including a porous substrate and an adhesive porous layer that is formed on at least one side of the porous substrate and contains a polyvinylidene-fluoride-based resin, the separator for a nonaqueous secondary battery being characterized in that the adhesive porous layer has a crystal size of 1 nm or more and 13 nm or less.

2. The separator for a nonaqueous secondary battery according to 1 above, characterized in that the weight of the adhesive porous layer formed on one side of the porous substrate is 0.5 g/m² or more and 1.5 g/m² or less.

3. The separator for a nonaqueous secondary battery according to 1 or 2 above, characterized in that the adhesive porous layer is formed on both front and back sides of the porous substrate.

4. The separator for a nonaqueous secondary battery according to 3 above, characterized in that the total weight of the adhesive porous layers formed on both sides of the porous substrate is 1.0 g/m² or more and 3.0 g/m² or less, and the difference between the weight of the adhesive porous layer on one side and the weight of the adhesive porous layer on the other side is 20% or less of the total weight.

5. The separator for a nonaqueous secondary battery according to any one of 1 to 4 above, characterized in that the value obtained by subtracting the Gurley value of the porous substrate from the Gurley value of the separator for a nonaqueous secondary battery with the adhesive porous layer formed thereon is 300 sec/100 cc or less.

6. The separator for a nonaqueous secondary battery according to any one of 1 to 5 above, characterized in that the porous substrate is a polyolefin microporous membrane containing polyethylene.

7. The separator for a nonaqueous secondary battery according to any one of 1 to 5 above, characterized in that the porous substrate is a polyolefin microporous membrane containing polyethylene and polypropylene.

8. The separator for a nonaqueous secondary battery according to 7 above, characterized in that the polyolefin microporous membrane includes at least two layers with one of the two layers containing polyethylene and the other layer containing polypropylene.

9. A nonaqueous secondary battery including the separator according to any one of 1 to 8 above.

Advantage of the Invention

[0013] According to the invention, it is possible to provide a separator for a nonaqueous secondary battery, which has better adhesion to electrodes compared with the prior art and is also capable of ensuring sufficient ion permeability even after attachment to an electrode. The use of the separator of the invention makes it possible to provide a high-energy-density, high-performance nonaqueous secondary battery having an aluminum laminate pack outer casing.

Mode for Carrying Out the Invention

[0014] The separator for a nonaqueous secondary battery of the invention includes a porous substrate and an adhesive porous layer that is formed on at least one side of the porous substrate and contains a polyvinylidene-fluoride-based resin. The separator for a nonaqueous secondary battery is characterized in that the adhesive porous layer has a crystal size of 1 nm or more and 13 nm or less. Hereinafter, the invention will be described in detail. Incidentally, a numerical range defined by "... to ..." hereinafter indicates a numerical range including the upper limit and the lower limit.

[Porous Substrate]

[0015] In the invention, a porous substrate refers to a substrate having pores or voids inside. Examples of such substrates include a microporous membrane, a porous sheet made of a fibrous material, such as a nonwoven fabric or a paper-like sheet, and a composite porous sheet made of such a microporous membrane or porous sheet and one or more other porous layers stacked thereon. Incidentally, a microporous membrane refers to a membrane having a large number of micropores inside, the micropores being connected to allow gas or liquid to pass therethrough from one side to the other side.

[0016] The material forming the porous substrate may be an electrically insulating organic material or inorganic material. In particular, in terms of imparting a shutdown function to the substrate, it is preferable to use a thermoplastic resin as a component of the substrate. Here, a shutdown function refers to the following function: in the case where the battery temperature increases, the thermoplastic resin melts and blocks the pores of the porous substrate, thereby blocking the movement of ions to prevent the thermal runaway of the battery. As the thermoplastic resin, a thermoplastic resin having a melting point of less than 200°C is suitable, and polyolefins are particularly preferable.

[0017] As a porous substrate using a polyolefin, a polyolefin microporous membrane is preferable. As the polyolefin microporous membrane, it is possible to use a polyolefin microporous membrane that has been applied to a conventional nonaqueous secondary battery separator, which has sufficient dynamic physical properties and ion permeability. Further, in terms of having the shutdown function mentioned above, it is preferable that the polyolefin microporous membrane contains polyethylene, and it is preferable that the polyethylene content is 95 wt% or more.

[0018] Separately, in terms of imparting heat resistance to such a degree that the membrane does not easily break when exposed to high temperatures, a polyolefin microporous membrane containing polyethylene and polypropylene is preferable. An example of such a polyolefin microporous membrane is a microporous membrane in which both polyethylene and polypropylene are present in one sheet. In terms of achieving both the shutdown function and heat resistance, it is preferable that the microporous membrane contains polyethylene in an amount of 95 wt% or more and polypropylene in an amount of 5 wt% or less. In addition, in terms of achieving both the shutdown function and heat resistance, it is also preferable that the polyolefin microporous membrane is a polyolefin microporous membrane having a laminate structure, which includes at least two layers with one of the two layers containing polyethylene and the other layer containing polypropylene.

[0019] It is preferable that the polyolefin has a weight average molecular weight of 100,000 to 5,000,000. When the weight average molecular weight is less than 100,000, it may be difficult to ensure sufficient dynamic physical properties. Meanwhile, when it is more than 5,000,000, shutdown characteristics may deteriorate, or it may be difficult to form a membrane.

[0020] The polyolefin microporous membrane can be produced by the following method, for example. That is, it is possible to employ a method in which a microporous membrane is formed by successively performing the following steps: (i) a step of extruding a molten polyolefin resin from a T-die to form a sheet, (ii) a step of subjecting the sheet to a crystallization treatment, (iii) a step of stretching the sheet, and (iv) a step of heat-treating the sheet. In addition, it is also possible to employ a method in which a microporous membrane is formed by successively performing the following steps: (i) a step of melting a polyolefin resin together with a plasticizer such as liquid paraffin and extruding the melt from a T-die, followed by cooling to form a sheet, (ii) a step of stretching the sheet, (iii) a step of extracting the plasticizer from the sheet, and (iv) a step of heat-treating the sheet.

[0021] As a porous sheet made of a fibrous material, it is possible to use a porous sheet made of a fibrous material containing a polyester such as polyethylene terephthalate, a polyolefin such as polyethylene or polypropylene, or a heat-resistant polymer such as aromatic polyamide, polyimide, polyethersulfone, polysulfone, polyether ketone, or polyetherimide, or a mixture of such fibrous materials.

[0022] A composite porous sheet may be configured to include a microporous membrane or a porous sheet made of a fibrous material and a functional layer stacked thereon. Such a composite porous sheet is preferable because a further function can be imparted by the functional layer. As a functional layer, for example, in terms of imparting heat resistance, it is possible to use a porous layer made of a heat-resistant resin or a porous layer made of a heat-resistant resin and an inorganic filler. The heat-resistant resin may be one or more kinds of heat-resistant polymers selected from aromatic polyamide, polyimide, polyethersulfone, polysulfone, polyether ketone, and polyetherimide. Examples of suitable inorganic fillers include metal oxides such as alumina and metal hydroxides such as magnesium hydroxide. Incidentally, examples of techniques for forming a composite sheet include a method in which a porous sheet is coated with a functional layer, a method in which they are joined together using an adhesive, and a method in which they are bonded together by thermocompression.

[0023] In the invention, in terms of obtaining good dynamic physical properties and internal resistance, it is preferable that the porous substrate has a thickness within a range of 5 to 25 μm . In terms of preventing a short circuit in the battery and obtaining sufficient ion permeability, it is preferable that the porous substrate has a Gurley value (JIS P8117) within a range of 50 to 800 sec/100 cc. In terms of improving production yield, it is preferable that the porous substrate has a

puncture resistance of 300 g or more.

[Polyvinylidene-Fluoride-Based Resin]

[0024] In the separator for a nonaqueous secondary battery of the invention, it is preferable to use a polyvinylidene-fluoride-based resin having a weight average molecular weight of 100,000 to 3,000,000. When a polyvinylidene-fluoride-based resin having a weight average molecular weight of less than 100,000 is applied, this tends to result in low adhesion strength to electrodes and thus is undesirable. In terms of adhesion strength, the weight average molecular weight is more preferably 500,000 or more. Meanwhile, when the weight average molecular weight is more than 3,000,000, a slurry containing the resin has high viscosity. As a result, it may be difficult to form an adhesive porous layer, or it may be impossible to form good crystals in the adhesive porous layer, making it difficult to obtain a preferred porous structure. Therefore, this is undesirable. In terms of such forming properties, the weight average molecular weight is more preferably 2,000,000 or less, and still more preferably 1,200,000 or less. Here, the weight average molecular weight of a polyvinylidene-fluoride-based resin can be determined by gel permeation chromatography (GPC method).

[0025] In the invention, as a polyvinylidene-fluoride-based resin, a homopolymer of vinylidene fluoride (i.e., polyvinylidene fluoride), a copolymer of vinylidene fluoride and another copolymerizable monomer, or a mixture thereof is used. As a monomer copolymerizable with vinylidene fluoride, for example, it is possible to use one or more kinds of tetrafluoroethylene, hexafluoropropylene, trifluoroethylene, trichloroethylene, vinyl fluoride, etc. It is preferable that the polyvinylidene-fluoride-based resin contains as a structural unit vinylidene fluoride in an amount of 70 mol% or more. Further, in terms of ensuring sufficient dynamic physical properties during joining to an electrode, a polyvinylidene-fluoride-based resin containing vinylidene fluoride in an amount of 98 mol% or more is preferable.

[0026] Such a polyvinylidene-fluoride-based resin having a relatively high molecular weight can be obtained preferably by emulsion polymerization or suspension polymerization, and particularly preferably by suspension polymerization.

[Adhesive Porous Layer]

[0027] In the invention, the crystal structure of the adhesive porous layer is an important technical factor. The crystal structure has a crystal size within a range of 1 to 13 nm. Here, an adhesive porous layer refers to a porous layer containing a polyvinylidene-fluoride-based resin and having a large number of micropores inside, the micropores being connected to allow gas or liquid to pass therethrough from one side to the other side. The crystal size can be calculated from the Scherrer equation shown in the following equation (1) using the Bragg angle and half-width of the peak at $2\theta = 20^\circ$ obtained by X-ray diffraction analysis.

$$D = K \times \lambda / \beta \cos \theta \quad \dots (1)$$

D: Crystal size

K: Scherrer constant

λ : X-ray wavelength

β : Half-width

θ : Bragg angle of diffraction line

[0028] In the adhesive porous layer, the amorphous part is responsible for adhesion, while pores are mainly responsible for ion permeability. In addition, the amorphous part also contributes to ion permeability. The crystalline part functions to maintain the structure during the heat pressing process or the like, but also serves as a factor that inhibits adhesion and ion permeability. In light of this, a structure in which crystals are finely and uniformly distributed allows for uniform attachment, whereby defects are reduced and good adhesion can be ensured, and thus is preferable. Further, in the structure in which crystals, which are a factor that inhibits the movement of ions, are finely and uniformly distributed, the movement of ions during charging and discharging is also uniform, resulting in good cycle characteristics or load characteristics. For this reason, the crystal size of the adhesive porous layer is preferably 1 to 13 nm, and more preferably 3 to 10 nm. In addition, when the crystal size is within such a range, the porous structure of the adhesive porous layer can be well maintained even after attachment to an electrode. Thus, the battery characteristics can be prevented from deterioration also in this respect. In addition, the invention is also greatly advantageous in that when the crystal size of the adhesive porous layer is within a range of 1 to 13 nm, good adhesion is exhibited regardless of the kind of electrode binder resin or electrolyte. According to such a separator, components of a battery can be selected from a wider variety of choices and combinations, making it possible to produce various nonaqueous secondary batteries.

[0029] Incidentally, in terms of uniformity, it is preferable that the crystal size is as small as possible. However, it is

practically difficult to form a porous structure of less than 1 nm, and, in terms of the ease of formation, it is preferable that the crystal size is 3 nm or more. Meanwhile, a crystal size of more than 13 nm leads to insufficient ion permeability after attachment and also makes it difficult to achieve uniform adhesion, resulting in the deterioration of battery characteristics. Therefore, this is undesirable. From such a point of view, the crystal size is more preferably 10 nm or less.

[0030] Several techniques can be mentioned as examples of methods for controlling the crystal size of the adhesive porous layer. For example, the temperature in a coagulation step for forming an adhesive porous layer is one factor. A decrease in this temperature tends to reduce the crystal size. In addition, the selection of a polyvinylidene-fluoride-based resin is another important factor. An increase in the molecular weight of the polyvinylidene-fluoride-based resin tends to reduce the crystal size, and when a polyvinylidene-fluoride-based resin having a weight average molecular weight of 500,000 or more is used, the suitable crystal size of the invention can be achieved relatively easily. In addition, the addition of a copolymer component to polyvinylidene fluoride reduces the crystal size. In terms of polymer structure, a polyvinylidene-fluoride-based resin in which CF_2 and CH_2 are randomly arranged has smaller crystal size, and such a polymer can be obtained more easily by emulsion polymerization than by suspension polymerization. In addition, a polyvinylidene-fluoride-based resin having a developed branched structure tends to have small crystal size, and one with wider molecular weight distribution tends to have smaller crystal size. Further, the composition of a coating liquid is another factor that controls the crystal size, and a decrease in the amount of phase-separation agent added to the coating liquid tends to reduce the crystal size.

[0031] The above methods for controlling crystal size are methods that suppress crystallization to inhibit the growth of crystal size. Apart from such methods, it is also possible to employ a technique in which a suitable nucleating agent is added to a coating liquid to greatly promote the crystallization rate, thereby inhibiting the growth of crystal size. Examples of suitable nucleating agents include metal oxides such as alumina and silica, metal hydroxides such as magnesium hydroxide, and other inorganic fillers. Considering the desired crystal size, it is preferable that the nucleating agent has a particle diameter of 10 nm or less, more preferably 5 nm or less. In the case of the configuration in which an inorganic filler is added, a slurry containing the inorganic filler dispersed in a coating liquid may be used in the formation of the adhesive porous layer. However, when an inorganic filler is incorporated into the adhesive porous layer, the adhesion to electrodes may decrease. Therefore, a configuration in which no inorganic filler is contained in the adhesive porous layer is preferable.

[0032] The controlling factors mentioned above are factors that also affect the formation of a porous structure, so it is undesirable to exert control only in terms of crystal size control. That is, it is preferable to determine the conditions in terms of both crystal size and porous structure. Naturally, the suitable ranges of conditions, such as the coating liquid composition and the coagulation temperature, vary depending on the resin selected, and thus the preferred range of each condition cannot be generally specified.

[0033] Incidentally, in the invention, for the purpose of improving the slidability and heat resistance of the separator, it is also possible to incorporate a filler made of an inorganic substance or organic substance or other additives into the adhesive porous layer. In such a case, it is preferable that the contents or particle sizes thereof are to such a degree that the effect of the invention is not inhibited. Examples of usable inorganic fillers include the metal oxides and metal hydroxides mentioned above. Examples of usable organic fillers include acrylic resin.

[Separator for Nonaqueous Secondary Battery]

[0034] As mentioned above, the separator for a nonaqueous secondary battery of the invention includes a porous substrate and an adhesive porous layer that is formed on at least one side of the porous substrate and contains a polyvinylidene-fluoride-based resin. Here, the adhesive porous layer is an adhesive layer to be attached, with an electrolyte contained therein, to an electrode by heat pressing. Therefore, it is necessary that the adhesive porous layer is present as the outermost layer of the separator. Naturally, in terms of cycle life, it is preferable that the separator is attached to both the positive electrode and the negative electrode. Therefore, it is preferable that the adhesive porous layer is formed on the front and back of the porous substrate.

[0035] In the invention, in terms of ion permeability, it is preferable that the adhesive porous layer has a structure that is sufficiently porous. Specifically, it is preferable that the value obtained by subtracting the Gurley value of the porous substrate from the Gurley value of the separator for a nonaqueous secondary battery with the adhesive porous layer formed thereon is 300 sec/100 cc or less, more preferably 150 sec/100 cc or less, and still more preferably 100 sec/100 cc or less. In the case where the difference is more than 300 sec/100 cc, the adhesive porous layer may be so dense that ion permeation is inhibited, whereby sufficient battery characteristics cannot be obtained.

[0036] In terms of obtaining sufficient battery performance, it is preferable that the separator for a nonaqueous secondary battery of the invention has a Gurley value within a range of 50 sec/100 cc or more and 800 sec/100 cc or less.

[0037] In order for the effect of the invention and the dynamic physical properties of the separator to be well obtained, a suitable range of the porosity of the separator for a nonaqueous secondary battery is 30% or more and 60% or less.

[0038] It is preferable that the weight of the polyvinylidene-fluoride-based resin is within a range of 0.5 to 1.5 g/m² on

one side. When the weight is less than 0.5 g/m^2 , the adhesion to electrodes may be insufficient. Meanwhile, a weight of more than 1.5 g/m^2 tends to inhibit ion permeability and deteriorate the load characteristics of the battery, and thus is undesirable. In the case where the porous layer made of a polyvinylidene-fluoride-based resin is formed on both front and back sides, it is preferable that the weight of the polyvinylidene-fluoride-based resin is 1.0 to 3.0 g/m^2 .

[0039] In the invention, in the case where the adhesive porous layer is formed on both sides of the porous substrate, the difference between the weight on the front side and the weight on the back side is also important. Specifically, it is preferable that the total weight of the adhesive porous layers formed on the front and back of the porous substrate is 1.0 to 3.0 g/m^2 , and the difference between the weight of the adhesive porous layer on one side and the weight of the adhesive porous layer on the other side is 20% or less of the total weight. When the difference is more than 20%, this may result in significant curling, interfering with handling or deteriorating cycle characteristics.

[Method for Producing Separator for Nonaqueous Secondary Battery]

[0040] The separator for a nonaqueous secondary battery of the invention mentioned above can be produced by a method in which a solution containing a polyvinylidene-fluoride-based resin is applied directly onto a porous substrate, and then the polyvinylidene-fluoride-based resin is solidified to integrally form an adhesive porous layer on the porous substrate.

[0041] Specifically, first, a polyvinylidene-fluoride-based resin is dissolved in a solvent to prepare a coating liquid. The coating liquid is applied onto a porous substrate, followed by immersion in a suitable coagulation liquid. As a result, the polyvinylidene-fluoride-based resin is solidified while inducing a phase-separation phenomenon. In this step, the polyvinylidene-fluoride-based resin layer has a porous structure. Subsequently, the porous substrate is washed with water to remove the coagulation liquid, followed by drying to integrally form an adhesive porous layer on the porous substrate.

[0042] For the coating liquid, a good solvent that dissolves the polyvinylidene-fluoride-based resin can be used. Examples of suitable good solvents include polar amide solvents such as N-methylpyrrolidone, dimethylacetamide, dimethylformamide, and dimethylformamide. In terms of forming a good porous structure, in addition to the good solvent, a phase-separation agent that induces phase separation is preferably mixed. Examples of phase-separation agents include water, methanol, ethanol, propyl alcohol, butyl alcohol, butanediol, ethylene glycol, propylene glycol, and tripropylene glycol. It is preferable that such a phase-separation agent is added within a range where viscosity suitable for coating can be ensured. In addition, in the case where a filler or other additives are incorporated into the adhesive porous layer, they may be mixed or dissolved into the coating liquid.

[0043] The composition of the coating liquid is preferably such that the polyvinylidene-fluoride-based resin is contained at a concentration of 3 to 10 wt%. In terms of forming a suitable porous structure, it is preferable that the solvent is a mixed solvent containing a good solvent in an amount of 60 wt% or more and a phase-separation agent in an amount of 40 wt% or less.

[0044] As the coagulation liquid, it is possible to use water, a mixed solvent of water and the good solvent, or a mixed solvent of water, the good solvent, and the phase-separation agent. In particular, a mixed solvent of water, the good solvent, and the phase-separation agent is preferable. In such a case, in terms of productivity, it is preferable that the mixing ratio between the good solvent and the phase-separation agent is determined according to the mixing ratio of the mixed solvent used for dissolving the polyvinylidene-fluoride-based resin. In terms of forming a good porous structure and improving productivity, it is preferable that the concentration of water is 40 to 90 wt%. In terms of controlling crystallinity, it is preferable that the coagulation temperature is about -20 to 60°C .

[0045] For the application of the coating liquid to a porous substrate, a conventional coating technique can be employed, such as Mayer bar, die coater, reverse roll coater, or gravure coater. In the case where the adhesive porous layer is formed on both sides of the porous substrate, it is possible that the coating liquid is applied to one side and then to the other, coagulated, washed with water, and dried. However, in terms of productivity, it is preferable that the coating liquid is applied to both sides of the porous substrate simultaneously, coagulated, washed with water, and dried.

[0046] Incidentally, in addition to the wet coating method mentioned above, the separator of the invention can also be produced by a dry coating method. Here, a dry coating method is a method in which the coating liquid containing a polyvinylidene-fluoride-based resin and a solvent is applied onto a porous substrate and then dried to remove the solvent by volatilization, thereby obtaining a porous membrane. However, in the case of a dry coating method, as compared with a wet coating method, it is more likely that the resulting coating is a dense membrane, and it is almost impossible to obtain a porous layer unless a filler or the like is added to the coating liquid. In addition, even when such a filler or the like is added, it is difficult to obtain a good porous structure. Therefore, from such a point of view, it is preferable to use a wet coating method in the invention.

[0047] In addition, the separator of the invention can also be produced by a method in which an adhesive porous layer and a porous substrate are separately produced, and then these sheets are stacked together and combined by thermo-compression bonding or using an adhesive, etc. The method for obtaining an adhesive porous layer as an independent sheet may be, for example, a method in which a coating liquid is applied onto a release sheet, then an adhesive porous

layer is formed by the wet coating method or dry coating method mentioned above, and only the adhesive porous layer is peeled off.

[Nonaqueous Secondary Battery]

[0048] The nonaqueous secondary battery of the invention is characterized by using the separator of the invention mentioned above.

[0049] In the invention, a nonaqueous secondary battery has a configuration in which the separator is placed between a positive electrode and a negative electrode, and these battery elements are enclosed in an outer casing together with an electrolyte. As the nonaqueous secondary battery, a lithium ion secondary battery is preferable.

[0050] As the positive electrode, a configuration in which an electrode layer made of a positive electrode active material, a binder resin, and a conductive additive is formed on a positive electrode current collector can be applied. Examples of positive electrode active materials include lithium cobalt oxide, lithium nickel oxide, lithium manganese oxide having a spinel structure, and lithium iron phosphate having an olivine structure. In the invention, in the case where the adhesive porous layer of the separator is placed on the positive-electrode side, because of the excellent oxidation resistance of the polyvinylidene-fluoride-based resin, there also is an advantage in that a positive electrode active material that can be operated at a high voltage of 4.2 V or more, such as $\text{LiMn}_{1/2}\text{Ni}_{1/2}\text{O}_2$ or $\text{LiCO}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3}\text{O}_2$, can be easily applied. Examples of binder resins include polyvinylidene-fluoride-based resins. Examples of conductive additives include acetylene black, ketjen black, and graphite powder. Examples of current collectors include an aluminum foil having a thickness of 5 to 20 μm .

[0051] As the negative electrode, a configuration in which an electrode layer made of a negative electrode active material and a binder resin is formed on a negative electrode current collector can be applied. A conductive additive may also be added to the electrode layer as necessary. Examples of usable negative electrode active materials are carbon materials capable of electrochemically storing lithium, materials capable of alloying with lithium, such as silicon and tin, and the like. Examples of binder resins include polyvinylidene-fluoride-based resins and styrene-butadiene rubber. The separator for a nonaqueous secondary battery of the invention has good adhesion. Therefore, sufficient adhesion can be ensured not only when a polyvinylidene-fluoride-based resin is used as a negative electrode binder, but also in the case of using styrene-butadiene rubber. In addition, examples of conductive additives include acetylene black, ketjen black, and graphite powder. Examples of current collectors include a copper foil having a thickness of 5 to 20 μm . In addition, instead of the negative electrode mentioned above, a metal lithium foil may also be used as a negative electrode.

[0052] The electrolyte has a configuration in which a lithium salt is dissolved in a suitable solvent. Examples of lithium salts include LiPF_6 , LiBF_4 , and LiClO_4 . Examples of suitable solvents include cyclic carbonates such as ethylene carbonate, propylene carbonate, fluoroethylene carbonate, and difluoroethylene carbonate, open-chain carbonates such as dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, and fluorine substitution products thereof, cyclic esters such as γ -butyrolactone and γ -valerolactone, and mixed solvents thereof. In particular, a solvent obtained by dissolving a lithium salt in a solvent containing cyclic carbonate/open-chain carbonate in a weight ratio of 20 to 40/80 to 60 at a concentration of 0.5 to 1.5 M is preferable. Incidentally, in a separator including a conventional adhesive porous layer, depending on the kind of electrolyte used, adhesion to electrodes is sometimes hardly exhibited. However, in the separator of the invention, good adhesion can be exhibited regardless of the kind of electrolyte. The invention is also greatly advantageous in this respect.

[0053] The separator for a nonaqueous secondary battery of the invention is applicable to a battery having a metal can outer casing. However, because of its good adhesion to electrodes, the separator of the invention is suitable for use in a soft pack battery having an aluminum laminate film outer casing. The method for producing such a battery is as follows. The positive electrode and negative electrode mentioned above are joined together via the separator, impregnated with an electrolyte, enclosed in an aluminum laminate film, and then heat-pressed, whereby a nonaqueous secondary battery can be obtained. This configuration of the invention allows the electrodes and the separator to be well attached together, making it possible to obtain a nonaqueous secondary battery having excellent cycle life. In addition, because of the good adhesion between the electrodes and the separator, the battery also has excellent safety. Examples of methods for joining the electrodes and the separator together include a stacking method in which the electrodes and the separator are stacked together and a method in which the electrodes and the separator are wound together. The invention is applicable to any of such methods.

Examples

[0054] Hereinafter, the invention will be described with reference to examples. However, the invention is not limited to the following examples.

[Measurement Method]

(Method for Measuring Crystal Size of Adhesive Porous Layer)

[0055] A polyvinylidene-fluoride-based resin peeled off from a separator was used as a sample and measured for crystal size by X-ray diffraction analysis. The measurement was performed using "NANO-Viewer" (manufactured by Rigaku) at 25°C by a transmission method. An imaging plate was used for detection. The two-dimensional data obtained using the imaging plate were converted into 2θ profiles, and the region at about 2θ = 8 to 30° was curve-fitted (gauss function/Lorentz function = 50/50). With respect to the peak at about 2θ = 20° separated by curve fitting, the Bragg angle and half-width were determined to calculate crystal size from the Scherrer equation shown in the following equation (2).

$$D = K \times \lambda / \beta \cos \theta \quad \dots (2)$$

D: Crystal size

K: Scherrer constant

λ: X-ray wavelength (CuKα is used as the target, so λ = 0.1542 nm)

β: Half-width

θ: Bragg angle of diffraction line

(Method for Measuring Membrane Thickness)

[0056] Measurement was performed using a contact thickness meter (LITEMATIC, manufactured by Mitutoyo). Using a cylindrical measuring terminal having a diameter of 5 mm, the thickness was measured with adjustment so that a load of 7 g was applied during the measurement.

(Weight per Unit)

[0057] A 10 cm x 10 cm sample was cut out and measured for weight. The weight was divided by the area to determine the weight per unit.

(Weight of Polyvinylidene-Fluoride-Based Resin)

[0058] Using an energy dispersion fluorescent X-ray analyzer (EDX-800HS, Shimadzu), the weight of a polyvinylidene-fluoride-based resin was measured from the intensity of the FKα spectrum. In the measurement, the weight of the polyvinylidene-fluoride-based resin on the X-ray irradiated side is measured. Therefore, in the case where a porous layer made of a polyvinylidene-fluoride-based resin is formed on both front and back sides, the front and back are each subjected to the measurement. Thus, the weight of the polyvinylidene-fluoride-based resin on each of the front and back sides is measured, and the weights are summed to determine the total weight on the front and back sides.

(Porosity)

[0059] The porosity ε (%) of a complex separator was calculated from the following equation 3.

$$\varepsilon = \{1 - (W_a / 0.95 + W_b / 1.78) / t\} \times 100 \quad \dots (3)$$

[0060] Here, W_a is the weight per unit of a substrate (g/m²), W_b is the weight of a polyvinylidene-fluoride-based resin (g/m²), and t is the membrane thickness (μm).

(Gurley Value)

[0061] Measurement was performed in accordance with JIS P8117 using a Gurley densometer (G-B2C, manufactured by Toyo Seiki Seisaku-Sho).

[Example 1]

[0062] KYNAR761 manufactured by ARKEM, polyvinylidene fluoride, was used as a polyvinylidene-fluoride-based resin. The polyvinylidene-fluoride-based resin was dissolved in a mixed solvent containing dimethylacetamide/tripropylene glycol in a weight ratio of 7/3 at a concentration of 6 wt% to prepare a coating liquid. Equal amounts of the coating liquid were applied respectively to both sides of a polyethylene microporous membrane (TN0901, manufactured by SK) having a thickness of 9 μm , a Gurley value of 160 sec/100 cc, and a porosity of 43%, followed by immersion in a coagulation liquid (20°C) containing water/dimethylacetamide/tripropylene glycol in a weight ratio of 57/30/13 to cause solidification. The microporous membrane was then washed with water, followed by drying to give a separator for a nonaqueous secondary battery according to the invention having an adhesive porous layer made of a polyvinylidene-fluoride-based resin on both front and back sides of the polyolefin-based microporous membrane. The separator was measured for the following properties: the crystal size of the adhesive porous layer (the crystal size of the PVdF-based resin), the thickness, weight per unit, and porosity of the separator, the weight of the adhesive porous layer (the total weight on both sides, the weight on the front side, the weight on the back side, and the percentage of the difference between the weight on the front side and the weight on the back side relative to the total weight on both sides), and the Gurley value of the separator. The results are shown in Table 1. Incidentally, the results from the separators of the following examples and comparative examples are also shown in Table 1.

[Example 2]

[0063] A separator for a nonaqueous secondary battery according to the invention was obtained in the same manner as in Example 1, except that a KF polymer W#1700 manufactured by Kureha Kagaku Kogyo, polyvinylidene fluoride, was used as a polyvinylidene-fluoride-based resin, and that the temperature of the coagulation liquid was 0°C.

[Examples 3 to 6]

[0064] Separators for a nonaqueous secondary battery according to the invention were obtained using the same coating liquid, the same polyethylene microporous membrane, and the same method as in Example 1, except that only the amount applied was changed as shown in Table 1.

[Examples 7 and 8]

[0065] Separators for a nonaqueous secondary battery according to the invention were obtained using the same coating liquid, the same polyethylene microporous membrane, and the same method as in Example 1, except that only the amounts applied to the front and back were changed as shown in Table 1.

[Example 9]

[0066] A separator for a nonaqueous secondary battery according to the invention was obtained in the same manner as in Example 1, except that a polyolefin microporous membrane (M824, manufactured by Celgard) having a three-layer structure including polypropylene/polyethylene/polypropylene with a thickness of 12 μm , a Gurley value of 425 sec/100 cc, and a porosity of 38% was used as a polyolefin microporous membrane.

[Example 10]

[0067] KYNAR761 manufactured by ARKEM, polyvinylidene fluoride, was used as a polyvinylidene-fluoride-based resin. The polyvinylidene-fluoride-based resin was dissolved in a mixed solvent containing dimethylacetamide/tripropylene glycol in a weight ratio of 8/2 at a concentration of 3.5 wt% to prepare a coating liquid. Equal amounts of the coating liquid were applied respectively to both sides of a polyethylene microporous membrane (TN0901, manufactured by SK) having a thickness of 9 μm , a Gurley value of 160 sec/100 cc, and a porosity of 43%, followed by immersion in a coagulation liquid (10°C) containing water/dimethylacetamide/tripropylene glycol in a weight ratio of 57/30/13 to cause solidification. Otherwise, in the same manner as in Example 1, a separator for a nonaqueous secondary battery according to the invention was obtained.

[Comparative Example 1]

[0068] A separator for a nonaqueous secondary battery was obtained in the same manner as in Example 1, except that the temperature of the coagulation liquid was 60°C.

[Comparative Example 2]

[0069] A polyvinylidene-fluoride-based resin having a copolymerization composition of vinylidene fluoride/hexafluoropropylene/chlorotrifluoroethylene in a weight ratio of 92.0/4.5/3.5 was produced by emulsion polymerization. The weight average molecular weight of the polyvinylidene-fluoride-based resin was 410,000. The polyvinylidene fluoride was dissolved in a mixed solvent containing dimethylacetamide/tripropylene glycol in a weight ratio of 60/40 at a concentration of 12 wt% to prepare a coating liquid. Equal amounts of the coating liquid were applied respectively to both sides of a polyethylene microporous membrane (TN0901, manufactured by SK) having a thickness of 9 μm , a Gurley value of 160 sec/100 cc, and a porosity of 43%, followed by immersion in a coagulation liquid (40°C) containing water/dimethylacetamide/tripropylene glycol in a weight ratio of 50/30/20 to cause solidification. The microporous membrane was then washed with water, followed by drying to give a separator for a nonaqueous secondary battery having an adhesive porous layer made of a polyvinylidene-fluoride-based resin on the polyolefin-based microporous membrane.

[Comparative Example 3]

[0070] Equal amounts of a 3 mass% dimethyl carbonate solution of a vinylidene fluoride/hexafluoropropylene copolymer (#8500, manufactured by Kureha Kagaku Kogyo) were applied respectively to both sides of a polyethylene microporous membrane (TN0901, manufactured by SK) having a thickness of 9 μm , a Gurley value of 160 sec/100 cc, and a porosity of 43%, and dried. However, the resulting coating was a dense membrane, and a separator for a nonaqueous secondary battery having an adhesive porous layer was not obtained. Incidentally, the Gurley value of the composite membrane was measured. The result was not less than 2,000 sec/100 cc, indicating significantly poor permeability.

[Production of Nonaqueous Secondary Battery]

(Production of Negative Electrode)

[0071] 300 g of artificial graphite (MCMB25-28, manufactured by Osaka Gas Chemicals) as a negative electrode active material, 7.5 g of "BM-400B" manufactured by Zeon (a water-soluble dispersion containing a modification product of a styrene-butadiene copolymer in an amount of 40 wt%) as a binder, 3 g of carboxymethylcellulose as a thickener, and an appropriate amount of water were stirred in a double-arm mixer to prepare a slurry for a negative electrode. The slurry for a negative electrode was applied to a copper foil having a thickness of 10 μm as a negative electrode current collector, and the resulting coating was dried, followed by pressing to prepare a negative electrode having a negative electrode active material layer.

(Production of Positive Electrode)

[0072] 89.5 g of a powder of lithium cobalt oxide (CELLSEED C, manufactured by Nippon Chemical Industrial) as a positive electrode active material, 4.5 g of acetylene black (DENKA BLACK, manufactured by Denki Kagaku Kogyo) as a conductive additive, and 6.0 g of polyvinylidene fluoride (KF polymer W#1100, manufactured by Kureha Kagaku Kogyo) as a binder were dissolved in NMP, and the resulting solution was stirred in a double-arm mixer in such a manner that the polyvinylidene fluoride was in an amount of 6 wt%, thereby preparing a slurry for a positive electrode. The slurry for a positive electrode was applied to an aluminum foil having a thickness of 20 μm as a positive electrode current collector, and the resulting coating was dried, followed by pressing to prepare a positive electrode having a positive electrode active material layer.

(Production of Battery)

[0073] A lead tab was welded to the positive electrode and the negative electrode. The positive and negative electrodes were then joined together via a separator, impregnated with an electrolyte, and enclosed in an aluminum pack using a vacuum sealer. Here, 1 M LiPF_6 ethylene carbonate/ethyl methyl carbonate (weight ratio: 3/7) was used as the electrolyte. The aluminum pack was then heat-pressed in a heat press at 90°C for 2 minutes while applying a load of 20 kg per cm^2 of electrode, thereby producing a test battery.

[Load Characteristic Test]

[0074] The load characteristic test was performed using nonaqueous secondary batteries produced as above. The relative discharge capacity at 2 C with respect to the discharge capacity at 0.2 C was measured at 25°C and used as an index of the load characteristics of a battery. The test was performed on batteries using the separators of Examples

1 to 8, Example 10, and Comparative Examples 1 and 2, respectively. The results are shown in Table 2.

[Charge-Discharge Cycle Test]

[0075] The charge-discharge cycle test was performed using nonaqueous secondary batteries produced as above. The charge condition was constant-current constant-voltage charge at 1 C and 4.2 V, while the discharge condition was constant-current discharge at 1 C to 2.75 V cut-off, and the cycle characteristics were thus tested. Here, capacity retention after 100 cycles was used as an index of cycle characteristics. The test was performed on batteries using the separators of Examples 1 to 8, Example 10, and Comparative Examples 1 and 2, respectively. The results are shown in Table 2.

[Check for Adhesion to Electrodes]

[0076] The batteries after the charge-discharge cycle test were each disassembled and checked for the adhesion between the separator and the electrodes. The adhesion was examined in terms of adhesion strength and uniformity. The results are shown in Table 2. Incidentally, in Table 2, adhesion strength on each of the positive-electrode side and the negative-electrode side is shown as a relative value taking the peel strength in the case of using the separator of Example 1 as 100. With respect to uniformity, after a peel test was performed on each of the positive-electrode side and the negative-electrode side, when almost the entire adhesive porous layer remained attached to the electrode surface, uniformity was rated as good (A); when most of the adhesive porous layer remained attached to the electrode surface, but the layer was partially broken, uniformity was rated as fair (B); and when most of the adhesive porous layer did not remain attached to the electrode surface, and the layer was significantly broken, uniformity was rated as poor (C).

[Heat Resistance Evaluation]

[0077] The heat resistance of the separator of Example 1 and that of the separator of Example 9 were compared by thermal mechanical analysis (TMA). Specifically, each separator was cut to a width of 4 mm, and both ends thereof were held in chucks and set to a chuck-to-chuck distance of 10 mm. Under an applied load of 10 mN, the temperature was raised at a temperature rise rate of 10°C/min, and the temperature at which the separator broke was measured. It was found that the separator of Example 1 broke at 155°C, while the separator of Example 9 broke at 180°C. This shows that the use of polypropylene is preferable in terms of heat resistance.

[Kind of Electrolyte and Adhesion]

[0078] The separators of Example 1 and Comparative Examples 1 and 2 were tested for adhesion to electrodes in the same manner as above using various electrolytes. Incidentally, 1 M LiPF₆ ethylene carbonate/ethyl methyl carbonate (weight ratio: 3/7) was used as an electrolyte A, 1 M LiPF₆ ethylene carbonate/propylene carbonate/ethyl methyl carbonate (weight ratio: 3/2/5) was used as an electrolyte B, and 1 M LiPF₆ ethylene carbonate/propylene carbonate (weight ratio: 1/1) was used as an electrolyte C. Table 3 shows the results. Incidentally, in Table 3, in terms of the average of the peel strengths on the positive electrode and the negative electrode expressed as relative values with respect to the peel strengths of the separator of Example 1 obtained on the positive electrode and the negative electrode, respectively, each taken as 100, an average of 70 or more is shown as Good, an average of 50 or more and less than 70 is shown as Fair, and an average of less than 50 is shown as Poor.

[Table 1]

	Crystal Size of PVdF-Based Resin (nm)	Thickness (μm)	Weight per Unit (g/m ²)	Porosity (%)	Weight of PVdF-Based Resin (g/m ²)				Gurley Value (sec/100 cc)
					Total	Front	Back	Difference between Front and Back	
Example 1	7.4	12	7.7	42	2.2	1.1	1.1	0%	248
Example 2	12.1	12	7.7	42	2.2	1.1	1.1	0%	235
Example 3	7.4	11	6.3	41	0.8	0.4	0.4	0%	218
Example 4	7.3	11	6.7	41	1.2	0.6	0.6	0%	226
Example 5	7.5	13	8.3	44	2.8	1.4	1.4	0%	273

(continued)

	Crystal Size of PVdF-Based Resin (nm)	Thickness (μm)	Weight per Unit (g/m^2)	Porosity (%)	Weight of PVdF-Based Resin (g/m^2)				Gurley Value (sec/100 cc)
					Total	Front	Back	Difference between Front and Back	
Example 6	7.2	14	8.7	44	3.2	1.6	1.6	0%	289
Example 7	7.4	12	7.7	42	2.2	1.3	0.9	18%	246
Example 8	7.3	12	7.7	42	2.2	1.6	0.6	45%	250
Example 9	7.5	14	9.6	35	2.0	1.0	1.0	0%	510
Example 10	3.1	13	7.7	50	2.2	1.1	1.1	0%	340
Comparative Example 1	15.8	15	7.7	52	2.2	1.1	1.1	0%	205
Comparative Example 2	16.9	14	7.5	50	2.0	1.0	1.0	0%	211

[Table 2]

	Results of Load Characteristic Test	Results of Charge-Discharge Cycle Test	Check for Adhesion to Electrodes			
			Positive Electrode		Negative Electrode	
			Adhesion Strength	Uniformity	Adhesion Strength	Uniformity
Example 1	95%	97%	100	A	100	A
Example 2	95%	96%	100	A	99	A
Example 3	95%	92%	85	A	72	A
Example 4	95%	95%	95	A	85	A
Example 5	93%	97%	103	A	113	A
Example 6	90%	96%	105	A	120	A
Example 7	94%	90%	104	A	90	A
Example 8	93%	79%	104	B	82	B
Example 10	85%	85%	98	A	95	A
Comparative Example 1	70%	63%	18	C	10	C
Comparative Example 2	68%	60%	15	C	5	C

[Table 3]

	Adhesion		
	Electrolyte A	Electrolyte B	Electrolyte C
Example 1	Good	Good	Good
Comparative Example 1	Poor	Fair	Good
Comparative Example 2	Poor	Fair	Good

Industrial Applicability

[0079] The nonaqueous secondary battery separator of the invention is suitable for use in a nonaqueous secondary battery. The separator is particularly suitable for use in a nonaqueous secondary battery having an aluminum laminate outer casing, where joining to electrodes is important.

Claims

1. A separator for a nonaqueous secondary battery, comprising a porous substrate and an adhesive porous layer that is formed on at least one side of the porous substrate and contains a polyvinylidene-fluoride-based resin, the separator for a nonaqueous secondary battery being **characterized in that** the adhesive porous layer has a crystal size of 1 nm or more and 13 nm or less.
2. The separator for a nonaqueous secondary battery according to claim 1, **characterized in that** the weight of the adhesive porous layer formed on one side of the porous substrate is 0.5 g/m² or more and 1.5 g/m² or less.
3. The separator for a nonaqueous secondary battery according to claim 1 or 2, **characterized in that** the adhesive porous layer is formed on both front and back sides of the porous substrate.
4. The separator for a nonaqueous secondary battery according to claim 3, **characterized in that** the total weight of the adhesive porous layers formed on both sides of the porous substrate is 1.0 g/m² or more and 3.0 g/m² or less, and the difference between the weight of the adhesive porous layer on one side and the weight of the adhesive porous layer on the other side is 20% or less of the total weight.
5. The separator for a nonaqueous secondary battery according to any one of claims 1 to 4, **characterized in that** the value obtained by subtracting the Gurley value of the porous substrate from the Gurley value of the separator for a nonaqueous secondary battery with the adhesive porous layer formed thereon is 300 sec/100 cc or less.
6. The separator for a nonaqueous secondary battery according to any one of claims 1 to 5, **characterized in that** the porous substrate is a polyolefin microporous membrane containing polyethylene.
7. The separator for a nonaqueous secondary battery according to any one of claims 1 to 5, **characterized in that** the porous substrate is a polyolefin microporous membrane containing polyethylene and polypropylene.
8. The separator for a nonaqueous secondary battery according to claim 7, **characterized in that** the polyolefin microporous membrane includes at least two layers with one of the two layers containing polyethylene and the other layer containing polypropylene.
9. A nonaqueous secondary battery comprising the separator according to any one of claims 1 to 8.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/074257

A. CLASSIFICATION OF SUBJECT MATTER H01M2/16(2006.01) i		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) H01M2/16, H01M4/13-H01M4/1399, H01M10/05-H01M10/0587		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2012 Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/098497 A1 (Teijin Ltd.), 02 September 2010 (02.09.2010), example 5-3; comparative example 5-2 & JP 2010-278018 A & JP 2011-77052 A & JP 4685974 B	1-9
A	JP 2003-171495 A (Teijin Ltd.), 20 June 2003 (20.06.2003), examples 1 to 8 & JP 2011-12266 A & US 2002/0197413 A1 & EP 1298740 A2 & CA 2403061 A & TW 252166 B & KR 10-2003-0027754 A & CN 1408466 A & KR 10-2009-0076860 A	1-9
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 16 January, 2012 (16.01.12)		Date of mailing of the international search report 24 January, 2012 (24.01.12)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/074257

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2006-120462 A (Sanyo Electric Co., Ltd.), 11 May 2006 (11.05.2006), entire text & US 2006/0088762 A1 & CN 1953268 A	1-9
A	JP 2007-317675 A (Teijin Ltd.), 06 December 2007 (06.12.2007), entire text & JP 4030312 B & US 2002/0197413 A1 & US 2003/0003363 A1 & US 2003/0017386 A1 & US 2005/0079406 A1 & EP 1191622 A1 & WO 2001/067536 A1 & DE 60143873 D & AU 4105401 A & CA 2373904 A & TW 531916 B & AU 779797 B & CN 1372706 A & CN 1591931 A & CA 2621132 A & AT 496399 T	1-9
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/074257

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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